Microscopic Energy Current Field with Multi–body Force in Hamiltonian System

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Abstract

Microscopic energy current can be derived from microscopic energy field localized only in particle positions. If the energy current is applied to classical molecular dynamics, it is expected to become a new information. However, multi–body force except two–body force causes obscurity when multi–body interaction energy is localized. In the present study, our new method enables to determine the localization of the multi–body interaction energy. We obtain the energy current between particles by the law of the multi–body force corresponding to Newton's third law on two–body force.

Keywords ; Energy current, Multi–body force, Molecular dynamics

1 Introduction

If a physical quantity and its flow exist, they need to be fields. The energy should be a field if the energy current is considerd. The total energy is, however, one quantity in the phase space. It is namely not the field. To accept the existence of the energy current, microscopic energy field is defined which all sort of the energy is localized only in particle positions. The energy current field is derived from the microscopic energy field. S. Lepri, R. Livi and A. Politi decided the energy current with the approximation of low–k limit [1]. S. Takesue derived the energy current field which satisfies strictly the 'continuity equation' with the microscopic energy field [2]. In his theory, the energy current field includes the term of the energy current between particles. The his theory differs from the one of J. H. Irving and G. Kirkwood [3] in the point that a distribution function is not required.

The microscopic energy field is not zero only at particle positions by the use of Dirac's delta function. The kinetic energy of each particle is naturally localized in the its particle position. Moreover, not only the kinetic energy but also the interaction energy is localized in particle positions. However, the interaction energy cannot be possessed by a single particle because the other party is necessary for the interaction. Historically, it was thought that both of two particles doing two–body interaction have just half the interaction energy.

If the theory of the microscopic energy field is expanded into a classical molecular dynamics (CMD), the energy current between particles can become a new information to analyze the dynamics of the particle. When particles are atoms and have covalent bonds, they are often subjected by the multi–body force in CMD. For the energy current, the multi–body interaction energy should be localized in the particle positions. The problem of the localization of the multi–body interaction energy is not as simple as the localization of the two–body interaction energy.

For example, let us consider a water molecule composed of two hydrogen atoms and an oxygen atom. Three–body interaction is often adopted to keep the angle between two covalent bonds 109.4 degree. The three–body interaction potential function depends on three atom positions. Therefore, the three–body interaction energy should be localized in the positions of the three atoms. One means of localization is to set one–third of the three–body interaction energy on each particles. However, we consider this means is not correct because the oxygen atom and the hydrogen atoms differ in their condition, both in the kind of atoms and the magnitude of the forces.

In another scene, such a problem of the localization the three–body interaction energy is discussed historically [4, 5, 6]. They argue the three particles has one–third of the three–body interaction energy. However they are groundless. In addition, the problem of the localization of the interaction energy has not been discussed when it is greater than three–body interaction.

In the present paper, we propose new method of the localization of the multi–body interaction energy into particle positions. The law of the multi–body force corresponding to Newton's third law is used.

The theory of the microscopic energy field and the energy current on a three dimensional space is introduced in section 2. We derive the energy current between particles according to only two–body force in section 3. In section 4, we describe the new method for the multi–body force. And, we discuss our new method in section 5.

2 Microscopic Energy Field and Energy Current

We introduce the derivation of microscopic energy field and microscopic energy current on Takesue's work[2]. The Hamiltonian of many–particle system is given by

$$\mathcal{H} = \sum_i \frac{\boldsymbol{p}_i{}^2}{2m_i} + U(\{\boldsymbol{x}\}), \tag{2.1}$$

where $\boldsymbol{p}_i$ and m_i are the i–th particle momentum and mass, $U(\{\boldsymbol{x}\})$ is the total interaction potential which depends on plural particle positions $\{\boldsymbol{x}\}$.

First, we consider the system of particles. The i–th particle energy $e_i(t)$ is localized in the i–th particle position $\boldsymbol{x}_i$. Thereby, the microscopic energy field $e(\boldsymbol{x}, t)$ is defined by

$$e(\boldsymbol{x}, t) = \sum_i e_i(t)\delta(\boldsymbol{x} - \boldsymbol{x}_i(t)), \tag{2.2}$$

where $\delta(\boldsymbol{x})$ is Dirac's delta function in three dimensional space as

$$\delta(\boldsymbol{x}) = \delta(x)\delta(y)\delta(z), \tag{2.3}$$

and

$$\boldsymbol{x} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{2.4}$$

The i–th particle kinetic energy $\boldsymbol{p}_i{}^2/2m_i$ is possessed by the i–th particle energy $e_i(t)$, and is not possessed by $e_k(t), (k \neq i)$. Moreover, we assume that the total interaction energy $U(\{\boldsymbol{x}\})$ is allocated into particles and is localized only in their positions. The interaction energy quota of the i–th particle is described by u_i. Therefore,

$$e_i(t) = \frac{\boldsymbol{p}_i(t)^2}{2m_i} + u_i(t). \tag{2.5}$$

A point to notice is that the interaction energy quota $u_i(t)$ is merely an artificial quantity. The differential of the interaction energy quota $u_i(t)$ cannot generate forces acting on particles. The differential of the total interaction potential $U(\{\boldsymbol{x}\})$ corresponds to the force. A main problem in the present paper is to determine the interaction energy quota $u_i(t)$. We describe the method to solve this problem in section 2 and 3.

Because the space integration of the microscopic energy field $e(\boldsymbol{x}, t)$ is equal to the total energy E in the system, we obtain the following condition for the i–th particle energy $e_i(t)$,

$$E = \int dx^3 e(\boldsymbol{x}, t) = \sum_i e_i(t). \tag{2.6}$$

The total energy E obeys energy conservation law.

If microscopic energy current field $\boldsymbol{j}(\boldsymbol{x}, t)$ exists, it satisfies the following 'continuity equation' with the microscopic energy field $e(\boldsymbol{x}, t)$;

$$\frac{\partial e(\boldsymbol{x}, t)}{\partial t} + \nabla \cdot \boldsymbol{j}(\boldsymbol{x}, t) = 0. \tag{2.7}$$

The time derivative of the $e(\boldsymbol{x}, t)$ becomes

$$\frac{\partial e(\boldsymbol{x}, t)}{\partial t} = \sum_i \frac{de_i(t)}{dt}\delta(\boldsymbol{x} - \boldsymbol{x}_i(t)) - \sum_i e_i(t)\dot{\boldsymbol{x}}_i(t) \cdot \nabla\delta(\boldsymbol{x} - \boldsymbol{x}_i(t)), \tag{2.8}$$

where, in three dimensional space, $\nabla\delta(\boldsymbol{x})$ is a column vector as

$$\nabla\delta(\boldsymbol{x}) = \begin{pmatrix} \frac{\partial}{\partial x}\delta(x)\delta(y)\delta(z) \\ \delta(x)\frac{\partial}{\partial y}\delta(y)\delta(z) \\ \delta(x)\delta(y)\frac{\partial}{\partial z}\delta(z) \end{pmatrix}. \tag{2.9}$$

When the i–th particle moves with velocity $\dot{\boldsymbol{x}}_i$, the energy current $e_i\dot{\boldsymbol{x}}_i$ is generated and is localized only in the i–th particle position $\boldsymbol{x}_i$ because the energy is localized only in particle positions as Eq.(2.2). Moreover, the energy current between particles is generated by the interaction between particles. From these point of view, we propose the microscopic energy current field $\boldsymbol{j}(\boldsymbol{x}, t)$ as follow;

$$\boldsymbol{j}(\boldsymbol{x}, t) = \sum_i e_i(t)\dot{\boldsymbol{x}}_i(t)\delta(\boldsymbol{x} - \boldsymbol{x}_i(t)) + \sum_{i,k>i} j_{i\to k}(t)\frac{\boldsymbol{\xi}_{ki}}{|\boldsymbol{\xi}_{ki}|}\delta(\boldsymbol{x}; \text{segment}, i \to k), \tag{2.10}$$

where $j_{i\to k}$ is the magnitude of the energy current from the i–th particle to the k–th particle, $\boldsymbol{\xi}_{ki}$ is relative position vector as

$$\boldsymbol{\xi}_{ki} \equiv \boldsymbol{x}_k - \boldsymbol{x}_i. \tag{2.11}$$

The localization function like the line segment from the i–th particle to the k–th particle is defined by

$$\begin{aligned}
&\delta(\boldsymbol{x};\mathrm{segment}, i \to k)\\
&\equiv (\boldsymbol{\xi}_{ki})_x\,|\boldsymbol{\xi}_{ki}|\,\delta\Big((\boldsymbol{\xi}_{ki} \times (\boldsymbol{x}-\boldsymbol{x}_i))_y\Big)\\
&\quad \times \delta\Big((\boldsymbol{\xi}_{ki} \times (\boldsymbol{x}-\boldsymbol{x}_i))_z\Big)\\
&\quad \times \theta\Big(\boldsymbol{\xi}_{ki}\cdot(\boldsymbol{x}-\boldsymbol{x}_i)\Big)\theta\Big(\boldsymbol{\xi}_{ik}\cdot(\boldsymbol{x}-\boldsymbol{x}_k)\Big),
\end{aligned} \tag{2.12}$$

where $(\cdots)_y$ and $(\cdots)_z$ are y– and z–components of a vector, and θ is the Heaviside step function. The first term of the right–hand in Eq.(2.10) means the energy current due to the movement of particles, and the second term is the energy current between particles owing to the interaction of particles.

The localization function $\delta(\boldsymbol{x};\mathrm{segment}, i \to k)$ has following property;

$$\begin{aligned}
&\frac{\boldsymbol{\xi}_{ki}}{|\boldsymbol{\xi}_{ki}|}\nabla\cdot\delta(\boldsymbol{x};\mathrm{segment}, i \to k)\\
&\qquad = \delta(\boldsymbol{x}-\boldsymbol{x}_i) - \delta(\boldsymbol{x}-\boldsymbol{x}_k).
\end{aligned} \tag{2.13}$$

From Eqs.(2.10) and (2.13), the divergence of the microscopic energy current field $\boldsymbol{j}(\boldsymbol{x},t)$ becomes

$$\begin{aligned}
\nabla\cdot\boldsymbol{j}(\boldsymbol{x},t) &= \sum_i e_i(t)\dot{\boldsymbol{x}}_i(t)\cdot\nabla\delta(\boldsymbol{x}-\boldsymbol{x}_i(t))\\
&\quad + \sum_{i,k\neq i} j_{i\to k}(t)\delta(\boldsymbol{x}-\boldsymbol{x}_i(t)),
\end{aligned} \tag{2.14}$$

where $j_{k\to i} = -j_{i\to k}$. The function $\delta(\boldsymbol{x}-\boldsymbol{x}_i(t))$ appears in second term of Eq. (2.14), because the energy current between particle exists only on the line segment between particles in (2.10). By comparison between Eqs. (2.8), (2.14), we obtain the condition for the energy current between particles

$$\frac{de_i(t)}{dt} = -\sum_{k\neq i} j_{i\to k}(t). \tag{2.15}$$

Thus, when the time derivative of the i–th particle energy $e_i(t)$ can be composed by summation $\sum_{k\neq i}$, we can regard the elements of the summation as the energy current between particles $j_{i\to k}$. Because the i–th particle energy $e_i(t)$ is defined by Eq. (2.5), We must determine the interaction energy quota $u_i(t)$ to obtain the energy current between particles $j_{i\to k}$.

3 Energy Current with Two–Body Force

We explain the interaction energy quota $u_i(t)$ according to two–body interaction. As a result, we obtain the energy current between particles $j_{i\to k}$. The two–body interaction potential function is described by $\phi_{ik}(r_{ik})$, where $r_{ik} \equiv |\boldsymbol{x}_i - \boldsymbol{x}_k|$. We set the following localization with the constants $a_i^{(ik)}$ and $a_i^{(ik)}$; the interaction energy localized in i–th particle position is $a_i^{(ik)}\phi_{ik}(r_{ik})$, and the interaction energy localized in k–th particle position is $a_k^{(ik)}\phi_{ik}(r_{ik})$. Thereby, the interaction energy quota u_i was defined by

$$u_i(t) \equiv {\sum_{k\neq i}}' a_i^{(ik)}\phi_{ik}(r_{ik}), \tag{3.1}$$

where ${\sum_{k\neq i}}'$ means summation about particles doing interaction with the i–th one.

From the right–hand of Eq. (3.1), the interaction energy quota u_i depends only on canonical variables. The kinetic energy ${\boldsymbol{p}_i}^2/2m_i$ is also composed only of canonical variables. Therefore, the i–th particle energy e_i is the function only of canonical variables, the Liouville operator can be applied to the time derivative of the i–th particle energy e_i as

$$\frac{de_i}{dt} = -\{H, e_i\} = -\sum_{k\neq i}\{e_k, e_i\}. \tag{3.2}$$

By comparison between Eqs. (2.15) and (3.2), the energy current from the i–th particle to the k–th one $j_{i\to k}$ is determined as the element of the summation in Eq. (3.2),

$$\begin{aligned}
j_{i\to k} &= \{e_k, e_i\}\\
&= \frac{\boldsymbol{p}_i}{2m_i}\cdot\frac{\partial u_k}{\partial \boldsymbol{x}_i} - \frac{\boldsymbol{p}_k}{2m_k}\cdot\frac{\partial u_i}{\partial \boldsymbol{x}_k}\\
&= \left(a_k^{(ik)}\frac{\boldsymbol{p}_i}{m_i} + a_i^{(ik)}\frac{\boldsymbol{p}_k}{m_k}\right)\cdot\frac{\partial\phi_{ik}(r_{ik})}{\partial \boldsymbol{x}_i}.
\end{aligned} \tag{3.3}$$

To explain the constants $a_i^{(ik)}$ and $a_k^{(ik)}$, let us consider the system of the two particles. The difference of the 1-st particle energy $e_1(t)$ between the times t_1 and t_2 is the follows from Eqs. (2.5) and (3.1);

$$\begin{aligned}
e_1(t_2) - e_1(t_1) &= \frac{\boldsymbol{p}_i(t_2)^2}{2m_i} - \frac{\boldsymbol{p}_i(t_1)^2}{2m_i}\\
&\quad + a_1^{(12)}\left[\phi_{12}(r_{12}(t_2)) - \phi_{12}(r_{12}(t_1))\right].
\end{aligned} \tag{3.4}$$

On the other hand, the difference of the 1-st particle energy $e_1(t)$ between the times t_1 and t_2 can

be described from Eqs. (2.15) and (3.3) by

$$\begin{aligned}
e_1(t_2) - e_1(t_1) &= -\int_{t_1}^{t_2} j_{1\to 2} dt \\
&= -\int_{t_1}^{t_2} \left(a_1^{(12)} + a_2^{(12)}\right) \frac{\boldsymbol{p}_1}{m_1} \cdot \frac{\partial \phi_{12}(r_{12})}{\partial \boldsymbol{x}_1} dt \\
&\quad + \int_{t_1}^{t_2} a_1^{(12)} \left(\dot{\boldsymbol{x}}_1 - \dot{\boldsymbol{x}}_2\right) \cdot \frac{\partial \phi_{12}(r_{12})}{\partial (\boldsymbol{x}_1 - \boldsymbol{x}_2)} dt \\
&= \left(a_1^{(12)} + a_2^{(12)}\right) \left(\frac{\boldsymbol{p}_i(t_2)^2}{2m_i} - \frac{\boldsymbol{p}_i(t_1)^2}{2m_i}\right) \\
&\quad + a_1^{(12)} \left[\phi_{12}(r_{12}(t_2)) - \phi_{12}(r_{12}(t_1))\right]. \quad (3.5)
\end{aligned}$$

For Eqs. (3.4) and (3.5), the constants satisfy

$$a_i^{(ik)} + a_k^{(ik)} = 1. \quad (3.6)$$

Because the both of two particles possess just half of the two–body interaction energy historically, the constants are determined by

$$a_i^{(ik)} = a_k^{(ik)} = \frac{1}{2}. \quad (3.7)$$

4 Energy Current with Multi–Body Force

We assume that the interaction energy was localized in particle positions even if the multi–body force appears. We abandon that the interaction energy quota u_i is directly proportionate to the multi–body interaction energy as is the case with the two–body interaction. We propose new method to determine the interaction energy quota u_i.

First, we explain the multi–body interaction potential. The total interaction potential $U(\{\boldsymbol{x}\})$ is the sum of the multi–body interaction potential. It can include the two–body interaction potential. However, it does not include the on–site potential. The necessary and sufficient condition to satisfy the total momentum conservation is that the multi–body interaction potential depends only on relative position vectors between particles $\{\boldsymbol{\xi}\}$ as

$$U(\{\boldsymbol{x}\}) = U(\{\boldsymbol{\xi}\}). \quad (4.1)$$

The multi–body force acting on the i–th particle due to the variation of the relative position vector between the i–th particle and the k–th one $\boldsymbol{\xi}_{ik}$ is described by $\boldsymbol{F}_i^{(ik)}$, and has the following property;

$$\begin{aligned}
\boldsymbol{F}_i^{(ik)} &= -\frac{\partial U(\{\boldsymbol{\xi}\})}{\partial \boldsymbol{\xi}_{ik}} \frac{\partial \boldsymbol{\xi}_{ik}}{\partial \boldsymbol{x}_i} \\
&= \frac{\partial U(\{\boldsymbol{\xi}\})}{\partial \boldsymbol{\xi}_{ki}} \frac{\partial \boldsymbol{\xi}_{ki}}{\partial \boldsymbol{x}_k} = -\boldsymbol{F}_k^{(ki)}. \quad (4.2)
\end{aligned}$$

It is namely that the forces acting on the i–th and k–th particles and the one with the variation of $\boldsymbol{\xi}_{ik}$ are equal in magnitude and opposite in direction. This is the law of the multi–body force corresponds to Newton's third law (the law of action and reaction). The total multi–body force acting on the i–th particle $\boldsymbol{F}_i$ is given by

$$\boldsymbol{F}_i = -\frac{\partial U(\{\boldsymbol{\xi}\})}{\partial \boldsymbol{x}_i} = \sum_{k\neq i} \boldsymbol{F}_i^{(ik)}. \quad (4.3)$$

Therefore, the Eq. (4.2) implies the total momentum conservation as

$$\begin{aligned}
\frac{d}{dt}\sum_i \boldsymbol{p}_i = \sum_i \boldsymbol{F}_i &= \sum_i \sum_{k\neq i} \boldsymbol{F}_i^{(ik)} \\
&= \sum_i \sum_{k>i} \left(\boldsymbol{F}_i^{(ik)} + \boldsymbol{F}_k^{(ki)}\right) \\
&= 0. \quad (4.4)
\end{aligned}$$

We consider a virtual frame which moves at a velocity $\boldsymbol{\beta}$ relative to the original frame as

$$\tilde{\boldsymbol{x}}_i(t) = \boldsymbol{x}_i(t) - \int^t \boldsymbol{\beta}(t')dt', \quad (4.5)$$

where quantities in the virtual frame are marked tilde as We define the interaction energy quota u_i as the negative work of the force acting on the i–th particle until time t in the virtual frame by

$$u_i(t) \equiv -\int^t \tilde{\boldsymbol{F}}_i(t') \cdot \dot{\tilde{\boldsymbol{x}}}_i(t')dt', \quad (4.6)$$

where $\tilde{\boldsymbol{F}}_i$ is the multi–body force acting on the i–th particle in the virtual frame as

$$\tilde{\boldsymbol{F}}_i = -\frac{\partial U(\{\tilde{\boldsymbol{\xi}}\})}{\partial \tilde{\boldsymbol{x}}_i}. \quad (4.7)$$

Relative position vectors and their derivatives are invariant under the virtual frame as

$$\tilde{\boldsymbol{\xi}}_{ik} = \boldsymbol{\xi}_{ik}, \quad (4.8)$$

$$\frac{\partial \tilde{\boldsymbol{\xi}}_{ik}}{\partial \tilde{\boldsymbol{x}}_l} = \frac{\partial \boldsymbol{\xi}_{ik}}{\partial \boldsymbol{x}_l} = \delta_{il} - \delta_{kl}. \quad (4.9)$$

Because the total interaction potential $U(\{\boldsymbol{\xi}\})$ depends only on the relative position vectors, it is invariant under the virtual frame as

$$U(\{\tilde{\boldsymbol{\xi}}\}) = U(\{\boldsymbol{\xi}\}). \quad (4.10)$$

Thereby, the multi–body forces are also invariant under the virtual frame as

$$\tilde{\boldsymbol{F}}_i^{(ik)} = -\frac{\partial U(\{\tilde{\boldsymbol{\xi}}\})}{\partial \tilde{\boldsymbol{\xi}}_{ik}} = -\frac{\partial U(\{\boldsymbol{\xi}\})}{\partial \boldsymbol{\xi}_{ik}} = \boldsymbol{F}_i^{(ik)}, \quad (4.11)$$

$$\tilde{\boldsymbol{F}}_i = \sum_{k\neq i} \tilde{\boldsymbol{F}}_i^{(ik)} = \sum_{k\neq i} \boldsymbol{F}_i^{(ik)} = \boldsymbol{F}_i. \quad (4.12)$$

For Eqs. (4.5) and (4.12), we can describe the interaction energy quota u_i of Eq. (4.6) by the quantities in the original frame as

$$u_i(t) = -\int^t \boldsymbol{F}_i(t') \cdot (\dot{\boldsymbol{x}}_i(t') - \boldsymbol{\beta}(t'))\, dt'. \quad (4.13)$$

From Eqs. (2.5), (4.13) and canonical equations of motion, the time derivative of the i–th particle energy e_i become

$$\frac{de_i}{dt} = \dot{\boldsymbol{p}}_i \cdot \frac{\boldsymbol{p}_i}{m_i} - \boldsymbol{F}_i \cdot \dot{\boldsymbol{x}}_i + \boldsymbol{F}_i \cdot \boldsymbol{\beta} = \boldsymbol{F}_i \cdot \boldsymbol{\beta}. \quad (4.14)$$

This implies that the energy current between particles $j_{i\to k}$ is generated in spite of satisfaction with the energy conservation law Eq. (2.6) from Eqs.(4.2) and (4.3) as

$$\begin{aligned} \frac{d}{dt}\sum_i e_i &= \sum_i \sum_{k>i} \left(\boldsymbol{F}_i^{(ik)} + \boldsymbol{F}_k^{(ki)} \right) \cdot \boldsymbol{\beta} \\ &= 0. \end{aligned} \quad (4.15)$$

Moreover, the plural virtual frame can be employed as long as the energy conservation Eq. (2.6) is satisfied. We apply different velocity $\boldsymbol{\beta}_{ik}$ in each force due to the variation of the relative position vector $\boldsymbol{\xi}_{ik}$. The interaction energy quota $u_i(t)$ is conclusively defined by

$$u_i(t) \equiv -\int^t \sum_{k\neq i} \boldsymbol{F}_i^{(ik)}(t') \cdot (\dot{\boldsymbol{x}}_i(t') - \boldsymbol{\beta}_{ik}(t'))\, dt', \quad (4.16)$$

where Eqs. (4.5) and (4.11) are used. This new definition (4.16) implies the change of the time derivative of the i–th particle energy $e_i(t)$ from Eq. (4.14) to

$$\frac{de_i}{dt} = \sum_{k\neq i} \boldsymbol{F}_i^{(ik)} \cdot \boldsymbol{\beta}_{ik}. \quad (4.17)$$

For the energy conservation law (2.6) and Eq. (4.2) give the following condition to determine the velocity $\boldsymbol{\beta}_{ik}$;

$$\begin{aligned} \frac{d}{dt}\sum_i e_i &= \sum_i \sum_{k\neq i} \boldsymbol{F}_i^{(ik)} \cdot \boldsymbol{\beta}_{ik} \\ &= \sum_i \sum_{k>i} \left(\boldsymbol{F}_i^{(ik)} \cdot \boldsymbol{\beta}_{ik} + \boldsymbol{F}_k^{(ki)} \cdot \boldsymbol{\beta}_{ki} \right) \\ &= \sum_i \sum_{k>i} \boldsymbol{F}_i^{(ik)} \cdot (\boldsymbol{\beta}_{ik} - \boldsymbol{\beta}_{ki}) \\ &= 0. \end{aligned} \quad (4.18)$$

This condition (4.18) implies that the velocity $\boldsymbol{\beta}_{ik}$ must be independent of the order of the subscripts i and k. The velocity $\boldsymbol{\beta}_{ik}$ has the dimension of the velocity, and depends on only the i–th and k–th particles. Therefore, we define

$$\boldsymbol{\beta}_{ik} = \boldsymbol{\beta}_{ki} \equiv c_i \dot{\boldsymbol{x}}_i + c_k \dot{\boldsymbol{x}}_k, \quad (4.19)$$

where the coefficients c_i and c_k are constants.

By comparison between Eqs. (2.15) and (4.17), the energy current from the i–th particle to the k–th one is determined by

$$j_{i\to k} \equiv -\boldsymbol{F}_i^{(ik)} \cdot (c_i \dot{\boldsymbol{x}}_i + c_k \dot{\boldsymbol{x}}_k)\,. \quad (4.20)$$

Moreover, when the total interaction potential $U(\{\boldsymbol{\xi}\})$ is composed of the two–body interaction, the energy current from the i–th particle to the k–th one $j_{i\to k}$ (4.20) should be consistent with Eq. (3.3). Therefore, all of the constants c_i and c_k are determined by

$$c_i = a_k^{(ik)} = \frac{1}{2}, \qquad c_k = a_i^{(ik)} = \frac{1}{2}. \quad (4.21)$$

The energy current from the i–th particle to the k–th one $j_{i\to k}$ is given by

$$j_{i\to k} \equiv -\frac{1}{2}\,(\dot{\boldsymbol{x}}_i + \dot{\boldsymbol{x}}_k) \cdot \boldsymbol{F}_i^{ik}. \quad (4.22)$$

5 Discussion

In present work, we extended the theory of the microscopic energy field and energy current to the system of the multi–body force. The i–th particle interaction energy quota u_i is defined by Eq. (4.16) as the negative work of the forces acting on the i–th particle until time t in the virtual frames moving at the velocity $\boldsymbol{\beta}_{ik}$ with each variation of relative position vector $\boldsymbol{\xi}_{ik}$. As a result, the energy current between particles $j_{i\to k}$ is obtained.

In the one particle system, the interaction potential is the negative work on the particle. By analogy with this, at first we defined the interaction energy quota u_i as the negative work of the force acting on the i–th particle until time t in the original frame by

$$u_i(t) \equiv -\int^t \boldsymbol{F}_i(t') \cdot \dot{\boldsymbol{x}}_i(t') dt', \quad (5.1)$$

where $\boldsymbol{F}_i(t)$ is the force acting on the i–th particle Eq. (4.3). From Eqs. (2.5), (5.1) and canonical equations of motion, the time derivative of the i–th particle energy e_i become

$$\frac{de_i}{dt} = \dot{\boldsymbol{p}}_i \cdot \frac{\boldsymbol{p}_i}{m_i} - \boldsymbol{F}_i \cdot \dot{\boldsymbol{x}}_i = 0. \quad (5.2)$$

Therefore, for the Eq. (2.15), the energy current between particles $j_{i\to k}$ becomes zero. The microscopic energy current field $\boldsymbol{j}(\boldsymbol{x}, t)$ is namely according to only movement of particles.

Now, in the macroscopic fluid dynamics, the energy current includes a stress term and a heat

current term besides the term of the movement of a fluid particle. If the microscopic energy field should be connected with the macroscopic field, the energy current between particles $j_{i\to k}$ need to be not zero. The definition (5.1) is regard as a failure.

We notice that the multi–body interaction potential and its forces are invariant under the transformation of a reference frame. The virtual frame moving at velocity $\boldsymbol{\beta}_{ik}$ relative to the original frame is used. As a result, the energy current between particles is generated. Although the time derivative of the i–th particle energy $e_i(t)$ (4.17) becomes not zero, the energy conservation law is satisfied owing to the law of the multi–body force (4.2) corresponding to Newton's third law as Eq. (4.18).

A problem is the determination of the constants $a_i^{(ik)}$, $a_k^{(ik)}$, c_i and c_k. When the interaction is due to the two–body force, it is suitable to split the two–body interaction energy into two particles just half as Eq.(3.7). The cause of the splitting half is not that two particles has same properties like a charge, a mass, a sort of atom, and so on. The cause must be that the forces on two particles are equal in magnitude due to Newton's third law. The constants c_i and c_k is also determined by 1/2 as Eq. (4.21) due to the law of the multi–body force (4.2) corresponding to Newton's third law.

Our method for the multi–body force yields new information $j_{i\to k}$ to the CMD. However, couples of the i–th and k–th particles for $j_{i\to k}$ depend on the selection of the independent variables $\{\boldsymbol{\xi}\}$ of the interaction potential $U(\{\boldsymbol{\xi}\})$. In the CMD under the multi–body force, we consider that the independent variables $\{\boldsymbol{\xi}\}$ are chosen as covalent bonds.

6 Conclusion

The theory of the microscopic energy field and the energy current was used with only two–body force. We propose the new method to deal with the multi–body force in the present paper. The interaction energy quota u_i in Eq. (2.5) is defined by Eq. (4.16). It means the negative work of the forces acting on the i–th particle until time t in the virtual frames moving at the velocity $\boldsymbol{\beta}_{ik}$ with each variation of relative position vector $\boldsymbol{\xi}_{ik}$. Then, the velocity $\boldsymbol{\beta}_{ik}$ is determined by Eq. (4.19). Our method is based on the law of the multi–body force Eq. (4.2) corresponding to Newton's third law. As a result, the theory of the microscopic energy field and the energy current is extended to the multi–body force. The energy current between particles $j_{i\to k}$ is derived as Eq. (4.22).

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